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(54) Title: CORROSION RESISTANT COATINGS CONTAINING AN AMORPHOUS PHASE

(57) Abstract

The disclosure relates to the forming of mineralized coatings on metal surfaces and to methods of forming such coatings. The coating can include a wide range of compounds and normally at least a portion of the coating corresponds to an amorphous phase. The coating and method are particularly useful in providing a corrosion resistant coating or film upon a metallic surface. This aspect of the disclosure involves the formation of a corrosion resistant "mineralized" layer of tailored composition upon a metal substrate.

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CORROSION RESISTANT COATINGS CONTAINING AN AMORPHOUS PHASE

10   CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part of United States Patent Application Serial Nos.
08/850,586 (Attorney Docket No. EL001RH-7) and 08/850,323 (Attorney Docket No. EL001RH-
6), filed on May 2, 1997; Serial Nos. 08/791,336 and 08/791,336, filed on January 31, 1997
(Attorney Docket No. EL001RH-4 and EL001RH-5); 08/634,215 (Attorney Docket No.
15   EL001RH-3), entitled "Corrosion Resistant Buffer System for Metal Products" and filed on April
18, 1996 in the names of Robert L. Heimann, et al., which is a continuation in part of US Patent
Application Serial No. 08/476,271 (Attorney Docket EL001RH-2) filed on June 7, 1995, which in
turn is a continuation-in-part of US Patent Application Serial No. 08/327,438 (Attorney Docket
EL001RH-1) filed on October 21, 1994, now allowed.   The disclosure of each of the previously
20   identified patent applications is hereby incorporated by reference.

                            FIELD OF THE INVENTION

The instant invention relates to the forming coatings on metal containing surfaces and to
methods of forming such coatings on a suitable substrate. The coating can include a wide range of
25   compounds and normally at least a portion of the coating corresponds to an amorphous phase. The
inventive coating and method are particularly useful in providing a corrosion resistant coating or
film upon a metallic surface. This aspect of the invention involves the formation of a corrosion
resistant "mineralized" layer of tailored composition upon a metal containing surfaces.

30   BACKGROUND OF THE INVENTION

The corrosion of steel and other metal containing products continues to be a serious
technical problem which has profound effects on the economy. Corrosion causes loss of natural
resources, and deteriorates key infrastructure such as roads and buildings.   It also causes
premature replacement of equipment and parts in industrial facilities, boats and other marine

5   vehicles, automobiles, aircraft, among a wide range of metallic components.

Current industry standards for corrosion prevention center around the use of barrier

coatings, sacrificial coatings, alloys containing heavy metals such as chromium, nickel, lead,

cadmium, copper, mercury, barium, among other heavy metals. The introduction of these

materials into the environment, however, can lead to serious health consequences as well as

10   substantial costs to contain or separate the materials or clean up environmental contamination.

Damage associated with corrosion, accordingly, is a continuing problem and better systems for

preventing corrosion are still needed.

A more detailed discussion of mineral containing materials can be found in Manual of

Mineralogy, by Dana, 21st edition, American Society of Metals, vol. 13, Corrosion in Structures,

15   "Reaction Sequence in Atmospheric Corrosion of Zinc ASTM STP 1239", by W. W. Kirk et al.,

and Physics and Chemistry of Mineral Surfaces, by Bradly (1996); the disclosure of each of the

aforementioned references is hereby incorporated by reference.

Conventional practices for improving protecting metal containing surfaces and imparting

improved surface characteristics to metals rely upon compositions and methods which are

20   undesirable as being costly or environmentally unsound.

SUMMARY OF THE INVENTION

The instant invention solves problems associated with conventional practices by providing

an improved method and a composition for improving the surface characteristics of a metal

25   containing surface. While the inventive composition is normally compatible with conventional

compositions and methods, the inventive composition can obviate the need to employ heavy metals

such as chrome and environmentally undesirable solvents.

The present invention in a broad aspect relates to compositions and methods for improving

or modifying the surface characteristics of a metal containing surface. In one aspect, the invention

30   involves methods for forming a "mineralized" layer upon the surface of a substrate. One method of

forming the mineralized layer comprises delivering precursors of the mineralized layer to the

surface of the metal surface via a carrier. The carrier can be a wide range of known compositions

such as a film forming composition, lubricants, gel, sealant, adhesive, paint, solvent and water-

borne resins, among other conventional compositions for forming coatings or films upon metals. If

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5   desired, the carrier can function as a reservoir of precursor materials thereby permitting additional

formation of the mineralized layer, e.g., when in the presence of a reservoir a breach in the

mineralized layer can be overcome by secondary mineral formation from mineral precursors in the

reservoir - a so-called self healing effect. If desired, the carrier can also function as a reservoir of

buffer materials, e.g., materials that passivate the pH of the metal surface, which can protect the

10   metal surface by providing an environment in which the metal is resistant to chemical attack.

Depending upon the utility of the carrier, the carrier can be removed or remain permanently in

contact with the mineralized surface (and at least a portion of the metal surface).

The instant invention provides an improved surface on articles by tailoring the surface

chemistry and effecting a new mineralized surface through chemical reaction and interaction.

15   The mineralized surface is formed when precursors are delivered to the surface of a metal or

metal coated articles or substrates. In some cases, the carrier includes materials which can

function to buffer the surface, as a precursor of the mineralized layer, alter pH, activate the

surface by changing the surface chemical species, or all of these functions. In some cases, the

surface mineralization is enhanced by a pretreatment step prior to application of the precursor-

20   containing carrier. After providing a proper environment, precursors can interact thereby in situ

forming the mineralized layer upon at least a portion of the metal surface. Depending upon the

surface environment, the metal or metal coated substrate can contribute donor ions to react and/or

interact with delivered precursors thereby forming a relatively thin mineralized layer that is

effective in altering and preferably enhance the characteristics of the entire article, e.g., by

25   altering and preferably enhancing the surface characteristics of the article. Consequently, the

instant invention permits tailoring a metal containing surface to possess improved corrosion,

coating adhesion, chemical resistance, thermal resistance, mechanical abrasion, acid rain

resistance, UV resistance, resistance to effects from atomic oxygen and vacuum UV, engineered

electrical resistance, among other improved properties. As will be described below in greater

30   detail, at least a portion of the mineralized coating or layer normally corresponds to a novel

amorphous phase.

DETAILED DESCRIPTION

The instant invention relates to compositions and methods for forming a mineralized

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5   coating or film upon at least a portion of a metal containing surface. By "mineralized" it is meant a

composition containing at least one member selected from the group of oxygenated cations and

anions wherein at least a portion of the mineral corresponds to an amorphous phase or matrix that

embeds or surrounds an inorganic complex oxide crystal. Normally, the amorphous phase is the

predominate phase component of the mineralized layer and, in some cases, substantially transparent

10   to visible light. This type of predominately amorphous structure is characterized by continuous

random network (CRN). In general, the mineral layer has a network structure in which metal atoms

are bound to oxygen atoms by predominantly covalent bonds. The CRN or network can be

modified by the introduction of metal oxides which are, in many embodiments of the invention,

contributed by the substrate. By "metal containing surface", "substrate", or "surface" it is meant to

15   refer to a metallic article and any metal containing surface as well as any substrate at least partially

coated with a metal layer, film or foil including a non-metallic article having a metal layer. A wide

variety of substances can be employed as precursors of the mineralized layer, such as one or more

cations of the metals of Groups I, II and III, and the transition metals, of the Periodic Chart of the

Elements. Additionally, one or more of the anions selected from the group consisting of water

20   soluble salts and/or oxides of tungsten, molybdenum, chromium, titanium, zircon, vanadium,

phosphorus, aluminum, iron, boron, bismuth, gallium, tellurium, germanium, antimony, niobium

(also known as columbium), magnesium and manganese, mixtures thereof, among others.

Particularly desirable results can be obtained by using salts and oxides of silicon, aluminum and

iron.

25   At least a portion of the resulting mineralized layer having oxide network attributes can be

characterized by the following formula:

$$A_x B_y O_z - nH_2O$$
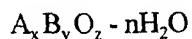
where A is termed a modifier cation and may be one or more ions selected from Group I, II and/or

III metals, and B is a network forming cation, such as silicon, aluminum, iron or magnesium. The

30   values of x and y can be any number except zero but x and y cannot all concurrently be zero and z

cannot be zero. "z" can have any value ranging from y to 4y. "n" is water of hydration and has a

value of from about 0 to about 10. The relationships of x, y, and z follow rules by Zachariasen in

the Journal of the American Chemical Society, Volume 54, page 3841 (1932); hereby incorporated

by reference:

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1). A high proportion of (network-forming cations are surrounded by oxygen tetrahedra or triangles.

2). The oxygen polyhedra only share corners with each other.

3) Some oxygen atoms are linked to only two cations, and do not form additional bonds with any other cations.

In one aspect of the invention, the complex inorganic crystals that are surrounded by or incorporated within the amorphous matrix to form the mineral layer can also be characterized by the following formula:

$$Mx\ (Si2O7)_A(SiO3)_B(Si4O11)_C(Si4O10)D(OH)_S * nH2O$$
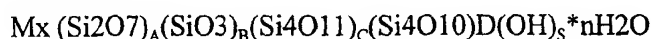
wherein Mx is one or more metals supplied by the previously described substrate and x ranges from 1 to 5; A + B + C + D = 1 wherein A, B, C and D can each individually equal zero but cannot simulataneosly be zero; n is the water of hydration and ranges from 0 to 10 and typically ranges from 0 to 6; and "s" is an interger that ranges from about 0 to about 4.

In another aspect of the invention, at least a portion of the crystalline component of the mineral layer that is surrounded or incorporated within the amorphous phase comprises:

$$M_x M'_y M''_z\ (SiO_4)_t(Si2O7)u(OH)2(A)_w\ (A')_v - nH_2O$$

where M, M', and M" are ions of Group I, II and/or III metals, and A and A' are the previously defined anions and where x, y, a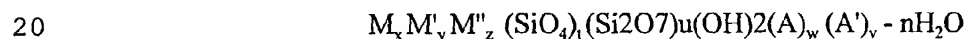nd z each can be any number including zero but x, y and z cannot all concurrently be zero. Analogously, t, u, v, w and x can each be any number including zero but cannot all concurrently be zero. "n" is the water of hydration and normally ranges from about 0 to about 10. At least one of M, M' and M" is a metal supplied from the substrate in contact with the mineralized layer, and normally up to two of M, M' or M" corresponds to an alkali or alkaline earth metal, e.g, calcium, potassium, sodium and mixtures thereof. For example, when the metal substrate comprises zinc and a precursor comprises sodium silicate the crystalline component, which is embedded within the amorphous matrix to form the mineralized layer, comprises $Zn_xNa_yMz(SiO4)_t(Si2O7)_u(OH)_2 * nH_2O$.
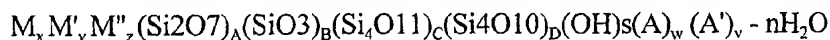
In a further aspect of the invention, at least a portion of the crystalline component of the mineral layer that is surrounded or incorporated within the amorphous phase comprises:

$$M_x M'_y M''_z(Si2O7)_A(SiO3)_B(Si_4O11)_C(Si4O10)_D(OH)s(A)_w\ (A')_v - nH_2O$$

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where M, M', and M" are ions of Group I, II and/or III metals, and A and A' are the previously defined anions and where v, w, x, y, and z each can be any number including zero but x, y and z cannot all concurrently be zero. Analogously, A, B, C and D can each be any number including zero but cannot all concurrently be zero. "n" is the water of hydration and normally ranges from about 0 to about 10; and typically, ranges from about 0 to 6. "S" is an interger that ranges from about 0 to about 4. At least one of M, M' and M" is a metal supplied from the substrate in contact with the mineralized layer, and normally up to two of M, M' or M" corresponds to an alkali or alkaline earth metal, e.g, calcium, potassium, sodium and mixtures thereof. Without wishing to be bound by any theory or explanation, it is believed that the presence of alkali cations, e.g, M", can influence the presence of other metal ions, e.g., M' supplied from the metal substrate, by an exchange or a replacement mechanism. For example, when the metal substrate comprises zinc and a precursor comprises sodium silicate the crystalline component, which is embedded within the amorphous matrix to form the mineralized layer, comprises $Zn_xNa_yMz(Si2O7)_A(OH)_S*nH_2O$.

The mineralized layer is formed from precursors. By "precursors" it is meant any combination of materials which interact with the metal surface or substrate to form the mineralized layer as well as intermediate products that interact further to form the mineralized layer. Examples of precursors include buffers such as silicate buffers and carbonate buffers including sodium hydroxide; alkali silicates such as at least one of sodium, calcium and potassium silicate; silica; cations supplied or delivered to the surface such as at least one of zinc, molybdenium; ions supplied or delivered to the surface such as at least one of oxygen, sulfur or chlorine from the environment surrounding the precursors or surface; compounds which decompose or react to form a precursor or intermediate thereof; mixtures thereof, among others. Depending upon the precursors, amount thereof and contact conditions, a silica containing layer may form upon the mineralized layer.

The mineralized layer can be tailored by adding one or more dopants to the precursor. Examples of suitable dopants comprise at least one member from the group consisting of anions selected from the group consisting of water soluble salts and/or oxides of tungsten, molybdenum, chromium, titanium, zircon, vanadium, phosphorus, aluminum, iron, boron, bismuth, gallium, tellurium, germanium, antimony, niobium (also known as columbium), magnesium and manganese, mixtures thereof, among others, and more especially, salts and oxides of aluminum and iron. Desirable results can be obtained by adding one or more dopants to a sodium silicate

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5   precursor.

The precursors of the mineralized layer are added to any suitable carrier. Examples of suitable carriers include hydrocarbons such as at least one member selected from the group consisting of animal, vegetable, petroleum derived and synthetic oils such as polyalphaolefin (PAO), silicone oil, phosphate esters, fluorinated oils such as KRYTOX (supplied by the DuPont

10   Company). Further examples of suitable carriers comprise at least one member selected from the group consisting of thermoplastic, thermosetting, cross-linked system, mixtures thereof, among others. Specific examples of such carriers include epoxies, acrylics, polyurethanes, silicones, polyesters, alkyds, vinyls, phenolics, fluoropolymers, latexes, mixtures thereof, among others. Depending upon the process conditions, the precursor carrier may be selected from alkylated

15   aromatics, phosphate esters, perfluoroalkylpolyethers, polyesters, olefins, chlorotrifluoroethylene, silahydrocarbons, phosphazenes, dialkylcarbonates, oligomers, polybutenes, and polyphenyl esters, as well as unsaturated polyglycols, silicones, silicate esters, cycloaliphatic hydrocarbons, and dibasic acid esters, e.g., when applying a precursor carrier to an iron containing surface a polyalphaolefin base oil having a kinematic viscosity in the range of about 30 - 1,400 centistokes at

20   40°C can be employed. Other properties to consider when choosing an appropriate polyalphaolefin base oil are molecular weight, molecular branching, thermal stability, and hydrophobicity, depending on the application. The polyalphaolefin base oil can be thickened to a gel with thickeners known to the art of grease manufacturers such as polytetrafluoroethylene or silica. Buffer materials are also suitable as thickeners as long as they are compatible with the base oil.

25   Generally, low molecular weight, synthetic, hydrocarbon oils provide greater ease in designing and manufacturing a gel with particular desired characteristics but are more costly than less refined, high molecular weight, petroleum hydrocarbon oils. Less refined hydrocarbons may also have the disadvantage of containing sulfide compounds which can feed sulfate reducing bacteria and, in turn, tend to corrode metals such as steel, iron and iron alloys.

30   The carrier film or layer can have a thickness of about 1 to at least about 50 mils, and typically has a thickness of about 1 to about 1.5 mil, e.g., about 0.2 to at least 0.4 mil. Normally, the carrier is semipermeable thereby permitting anions from the surrounding environment to contact precursors to the mineralized product. By "semipermeable" it is meant to refer to a microporous structure, either natural or synthetic allowing passage of ions, water and other solvent

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5   molecules, and very small other molecules. The resin can be essentially insoluble in water and resistant to macro-penetration by flowing water. The resin layers, however, are normally permeable to water molecules and inorganic ions such as metal ions and silicate ions.

The amount of mineralized layer precursor present in the carrier typically comprises about 1 to about 60 wt.% of the carrier, e.g, normally about 5 to about 10 wt.% depending upon the carrier.

10   The mineralized layer precursors can be combined with the carrier in any suitable conventional manner known in this art.

The mineralized layer precursors can include or be employed along with one or more additives such as the pH buffers such as those listed below in Tables A and B, mixtures thereof, among others. In some cases, a buffer also functions as a precursor, e.g., sodium silicate. The

15   amount of these additives typically ranges from about 1 to about 60 wt.% of the carrier, e.g., normally about 5 to about 10 wt.%. These additives can be added to the carrier in order to tailor the characteristics of the mineralized layer, the carrier itself, upon a pre-treated surface, among other characteristics. By adding suitable mineralized layer precursors, carrier, additives, among other materials, the surface of the metal containing layer can be tailored by forming a mineralized layer to

20   possess improved corrosion resistance, adhesion, among other characteristics.

Table A - Examples of Buffering Compounds

Chemical Name	Formula
Boric Acid	H_3BO_3
Citric Acid	$H_3C_6H_5O_7 \cdot H_2O$
Sodium Hydroxide	NaOH
Trisodium Phosphate Dodecahydrate	$Na_3PO_4 \cdot 12H_2O$
Potassium Silicate	SiO_2/K_2O 1.6-2.5 wt. Ratio
Sodium Silicate	SiO_2/Na_2O 2.0-3.22 wt. Ratio

Chemical Name	Formula
Potassium Hydrogen Phthalate	$KHC_8O_4H_4$
Potassium Dihydrogen Phosphate	KH_2PO_4
Borax	$Na_2B_4O_7$
Sodium Hydrogen Carbonate	$NaHCO_3$
Disodium Phosphate Dodecahydrate	$Na_2HPO_4 \cdot 12H_2O$
Sodium Acetate	$NaOOCCH_3$
Disodium Phosphate	Na_2HPO_4

Table B - Examples of Weight Ratios of Buffering

Components for Various pH Values

Desired pH	Weight	Chemical	Weight	Chemical	Weight	Chemical
3.0	1.00	Boric Acid	0.84	Citric Acid	0.18	Trisodium Phosphate
3.5	1.00	Boric Acid	0.84	Citric Acid	.027	Trisodium Phosphate
4.0	1.00	Sodium Hydroxide	196.00	Potassium	Hydrogen	Phthalate

Desired pH	Weight	Chemical	Weight	Chemical	Weight	Chemical
4.5	1.00	Sodium Hydroxide	29.30	Potassium	Hydrogen	Phthalate
5.0	1.00	Sodium Hydroxide	11.30	Potassium	Hydrogen	Phthalate
5.5	1.00	Sodium Hydroxide	6.97	Potassium	Hydrogen	Phthalate
6.0	1.00	Sodium Hydroxide	30.40	Potassium	Dihydrogen	Phosphate
6.5	1.00	Sodium Hydroxide	12.20	Potassium	Dihydrogen	Phosphate
7.0	1.00	Sodium Hydroxide	5.84	Potassium	Dihydrogen	Phosphate
7.5	1.00	Sodium Hydroxide	4.14	Potassium	Dihydrogen	Phosphate
8.0	1.00	Sodium Hydroxide	3.64	Potassium	Dihydrogen	Phosphate
8.5	1.00	Boric Acid	0.84	Citric Acid	4.80	Trisodium Phosphate (12 H_2O)
9.0	1.00	Boric Acid	0.84	Citric Acid	5.82	Trisodium Phosphate (12 H_2O)
9.5	1.00	Sodium	13.55	Borax		

Desired pH	Weight	Chemical	Weight	Chemical	Weight	Chemical
		Hydroxide				
10.0	1.00	Sodium Hydroxide	6.52	Borax		
10.5	1.00	Sodium Hydroxide	5.25	Borax		
11.0	1.00	Sodium Hydroxide	2.31	Sodium	Hydrogen	Carbonate
11.5	1.00	Sodium Hydroxide	8.00	Disodium	Acid Phosphate (12H$_2$O)	
12.0	1.00	Sodium Hydroxide	1.30	Disodium	Acid Phosphate (12H$_2$O)	
12.5	1.00	Sodium Hydroxide	15.00	Disodium	Acid Phosphate	
13.0	1.00	Sodium Hydroxide	1.00	Sodium	Acetate	

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The aforementioned carrier can be applied to a metal containing surface by using any expedient method. Depending upon the desired results, the metal containing surface can be applied or reapplied as appropriate. Examples of suitable methods for applying the tailored carrier comprise at least one of painting, spraying, dipping, troweling, among other conventional methods.

10   By employing a suitable tailored carrier, the instant invention can form a mineralized layer to protect a metal containing surface having at least one member from the group of magnesium, aluminum, vanadium, calcium, beryllium, manganese, cobalt, nickel, copper, lead, copper, brass, bronze, zirconium, thallium, chromium, zinc, alloys thereof, among others. Particularly, desirable

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5   results can be obtained when forming a mineralized layer upon a zinc containing surface.

In an aspect of the invention, the metal containing surface comprises zinc which is contacted with a carrier including sodium silicate. The carrier can comprise PAO or polyurethane. The amount of sodium silicate within a PAO carrier typically ranges from about 1 to about 30 wt.%, e.g., about 5 to about 10 wt.%, whereas for a carrier comprising polyurethane the amount of

10   sodium silicate typically ranges from about 1 to about 15 wt.%, e.g., about 5 to about 10 with especially desirable results being obtained at about 6.5 wt.% sodium silicate. When the previously desired carrier is employed, desirable results can be obtained by applying one or more topcoats to the carrier, e.g., polyurethane, polytetrafluoroethylene, mixtures thereof, among others. The topcoat can function as a physical barrier to the surrounding environment thereby providing further

15   corrosion resistance. The thickness of the carrier layer including any topcoat normally ranges from about 0.75 to about at least about 1.5 mils. The corrosion resistance can be further enhanced by heat treating the coated metal surface. That is, after applying a silicate containing carrier to a zinc containing surface and allowing the carrier to incubate, the coated surface is heated (in any suitable atmosphere such as air), to a temperature of about 125 to about 175 C. Consequently, the instant

20   invention permits tailoring the carrier, mineralization precursors, topcoat as well as any heat treatment to obtain a predetermined corrosion resistance, e.g., in the case of a zinc containing surface the ASTM B117 resistance can range from 100 to 3,000 hours.

In an aspect of the invention, the metal containing surface comprises zinc which is contacted with a carrier including sodium silicate. The carrier can comprise PAO or polyurethane.

25   The amount of sodium silicate within a PAO carrier typically ranges from about 1 to about 30 wt. %, e.g., about 5 to about 10 wt. %, whereas for a carrier comprising polyurethane the amount of sodium silicate typically ranges from about 15 wt. %, e.g. about 5 to about 10 with especially desirable results being obtained at about 6.5 wt. % sodium silicate. When the previously desired carrier is employed, desirable results can be obtained by applying one or more topcoats to the

30   carrier, e.g., polyurethane, polytetrafluoroethylene, mixtures thereof, among others. The topcoat can function as a physical barrier to the surrounding environment thereby providing further corrosion resistance. The thickness of the carrier layer including any topcoat normally ranges from about 0.75 to about at least about 1.5 mils. The corrosion resistance can be further enhanced by heat treating the coated metal surface. That is, after applying a silicate containing carrier to a zinc

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5   containing surface and allowing the carrier to incubate, the coated surface is heated (in any suitable
atmosphere such as air), to a temperature of about 125 to about 175 C. Consequently, the instant
invention permits tailoring the carrier, mineralization precursors, topcoat as well as any heat
treatment to obtain a predetermined corrosion resistance, e.g., in the case of a zinc containing
surface the ASTM B117 resistance can range from 100 to 3,000 hours.

10   Without wishing to be bound by any theory or explanation, it is believed that the
mineralized layer is formed under a variety of chemical and physical forces including 1)
transporting ions through the carrier via osmotic pressure and diffusion thereby providing ions to
the metal surface, 2) oxygen deprived environment, 3) buffering to provide a predetermined
alkaline pH environment that is effective for formation of the mineralized layer upon a given metal

15   surface, e.g, in the case of a zinc containing surface about 9.5 to at least about 10.5 pH, 4)
heterogenious process using any available ions, 5) water present at the surface, in the carrier or as a
reaction product can be removed via heat, vacuum or solvent extraction, 6) using a reservoir
adjacent to the metal surface that can control that ion transport rate as well as the rate of water (and
moieties) passing through the reservoir and serve to provide, as needed, a continuous supply

20   mineralized layer precursors, among other forces.

               The process for forming the inventive mineralized layer can be initiated by delivering
buffering ions of combinations or single component alkali metal polyoxylates (for example
sodium silicate) to passivate the metal surface, e.g., refer to item 3) in the previous paragraph. In
the case of sodium silicate, the carrier contains dissolved silica in the form of a silicate anion in

25   water as well as sodium oxide in the form of sodium hydroxide in the presence of water. If
desired, sodium hydroxide can be employed maintaining the pH of the solution in a range where
the silicate can remain soluble. In the case of other substrates and other anion systems, the
buffering capacity of the reactants is designed to passivate the surface, manage the pH of the
surface chemistry, activate the surface, oxidize the surface, or to prepare or condition the surface

30   for a mineral-forming reaction or any combination of the above. The delivery of ions is through
a carrier comprising a membrane employing osmotic pressure to drive precursors to the surface.

               The ionic species, which are present in the carrier or that pass through the
carrier/membrane, can then interact chemically and can become associated with the surface of the
metal to form a submicron mineralization layer, e.g., a monolayer. In the present invention these

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5   interactions occur adjacent to or upon the surface of the substrate to form a mineralized layer. It

is to be understood that the aforementioned membrane is associated with creating an oxygen-

limited passivation environment as part of the mineralization process.

       Moreover, the mineralized layer precursors can interact in such a manner to produce

mineralized layer in-situ at the surface. Depending upon the conditions of the surface, the

10   substrate may contribute precursors in the form of metal ions. The metal ions of the substrate

surface may exist as oxides, or the ions may have reacted with chemical species in the

surrounding environment to form other metal species. In the case of a zinc substrate or surface,

zinc can oxidize in the environment existing at the surface as zinc oxide, but may also form zinc

carbonate from the exposure to carbon dioxide in the air. Under certain conditions, the zinc

15   carbonate will predominate the surface species of the precursor to form the mineralized surface.

In the case of other metal substrates, the ability of the surface to contribute ions to function as

mineral precursors can be achieved by conditioning the surface, e.g., to populate the surface with

oxide species that will participate as mineralized layer precursors.

       To enhance mineral layer formation on at least a portion of the surface of a metal

20   substrate, the metal surface may be prepared or pretreated. Metal surfaces normally tend to be

covered with a heterogeneous layer of oxides and other impurities. This covering can hinder the

effectiveness of the buffering and/or mineral layer formation. Thus, it becomes useful to convert

the substrate surface to a homogenous state thereby permitting more complete and uniform

mineral layer formation. Surface preparation can be accomplished using an acid bath to dissolve

25   the oxide layers as well as wash away certain impurities. The use of organic solvents and

detergents or surfactants can also aid in this surface preparation process. Phosphoric acid based

cleaners, such as Metal Prep 79 (Parker Amchem), fall into a category as an example commonly

used in industry. Other combinations of acids and cleaners are useful as well and are selected

depending upon the metal surface and composition of the desired mineral layer. Once the

30   surface is pretreated, the surface can then be subjected to further activation, if necessary, to

enhance the buffering capability, including but not limited to oxidation by any suitable method.

Examples of suitable methods comprise immersion in hydrogen peroxide, sodium peroxide,

potassium permanganate, mixtures thereof, among other oxidizers.

5   Depending upon the carrier and process condition, precursors can pass through the carrier

membrane system as anions, and interact adjacent to or upon the surface with metal cations,

which in most cases are donated by the metal surface or substrate to form a relatively thin

mineralized layer, e.g., a monolayer.   In one aspect of the invention, sodium silicate (as $SiO3$—

ion) reacts with a zinc containing surface, e.g., that exists primarily as zinc carbonate, to form an

10   amorphous mineralization layer containing a nanocrystaline hemimorphite phase that is normally

less than 100 Angstroms in thickness. In this aspect of the invention, the metal surface was

prepared for mineralization by the presence of a suitable buffering alkali, e.g., buffering with a

silicate to a pH in the range of about 9.5 to about 10.5. While a higher pH can be effectively

used, a pH of less than about 11 minimizes the need for certain relatively complex and expensive

15   handling procedures.

In another aspect of the invention, the delivery of pH buffering agents as well as the

anion reactants can be designed to tailor the surface characteristic. For example, in order to

achieve improved resistance to acid rain on a zinc surface, the silicate anions can be

complemented with zirconate anions. Further, in the case of an iron containing surface, the

20   carrier can deliver silicate anions to a anodically conditioned surface to form amorphous phase

comprising julgoldite.

In yet another aspect of the invention, a surface pretreatment was used to enhance the

mineralization layer formation. For example, in order to achieve an improved corrosion surface

on iron, the steel substrate was first treated with a phosphoric acid containing cleaner, then

25   exposed to an oxidizer in order to remove unwanted material and convert at least a portion of the

surface to a homogeneous species of iron oxide. The mineralized layer was then formed on the

pretreated metal surface by being contacted with sodium silicate containing precursor which in

turn can proceed to form a clinopyroxene of sodium iron silicate.

While any suitable buffer can be employed for practicing the invention, buffer solutions are

30   typically prepared by mixing a weak acid and its salt or a weak base and its salt. Acidic buffers, for

example, can be prepared using potassium chloride or potassium hydrogen phthalate with

hydrochloric acid of appropriate concentrations.   Neutral buffers can be prepared by mixing

potassium dihydrogen phosphate and sodium hydroxide, for example. Alkaline (basic) buffers can

be prepared by mixing borax or disodium hydrogen phosphate with sodium hydroxide, for

15

5   example. Many more chemical combinations are possible, using appropriate chemicals to establish the proper sequence of proton transfer steps coupled with the intended reactions. Buffer exchange rates may be modified by combinations of buffer materials that react at different ionic exchange rates; buffers of low-change type react more rapidly than high-change types.

Aqueous polymers are preferred carriers for buffers in liquid form and include water-

10   reducible alkyds and modified alkyds, acrylic latexes, acrylic epoxy hybrids, water reducible epoxies, polyurethane dispersions, vinyls and ethylene vinyl acetates, and mixtures thereof. Such polymers are water vapor permeable but are repellent of liquid water and are essentially water insoluble after curing. These polymers can form a semipermeable membrane for water vapor and ionic transfer. Hence, if the surface of the metal substrate is dry, water vapor can permeate the

15   membrane; but, buffering ions, which are present in the membrane or that pass through the membrane, can passivate the metal surface thereby reducing corrosion.

Buffer materials are chosen based on the type of the surface or substrate to be protected. Metal substrates may be protected from corrosion by passivating the substrate surface. Such passivation may generally be accomplished only in certain pH ranges which, in turn, depend on the

20   specific substrate to be protected. For example, iron based alloys are passivated with an alkaline pH (pH 8-12). This pH range is preferably accomplished with sodium silicate and/or potassium silicate powders; but other alkaline materials may be used. A blend of sodium and potassium silicates is also useful for achieving viscosity control in aqueous carrier/membrane formulations.

In a further aspect of the invention, a mineralized layer is obtained by mixing silicates

25   and anodic oxidizing materials such as sodium carbonate and delivering the mixture in a manner effective to activate the metal surface.

While the above description emphasizes a zinc containing surface, the surface of a wide range of metal surfaces can be altered to impart beneficial surface characteristics. In most cases, the substrate or the surface thereof contributes cations to the mineralization-forming reaction.

30   Examples of metal surfaces include aluminum, zinc, iron, copper, brass, iron, steel, stainless steel, lead, alloys thereof, among others. In the case of limited mineral layer formation or thickness of the mineral layer is caused by the surface contribution of the cation, an improved result can be obtained by managing or tailoring the pH. That is, the buffering capacity and the pH of the carrier is substrate surface-specific and is tailored to manage the surface chemistry to

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5   form the inventive mineralization layer, e.g., selecting a pH at which the surface is reactive

encourages formation of the mineralization layer. The reaction for forming the new surface with

continue until such time that the finite quantity of metal atoms at the surface are consumed. If

the new mineralized layer is marred or destroyed, a desirable aspect of the instant invention is

that the surface will reinitiate mineralization formation with any available precursors. The ability

10   to reinitiate mineralization or self-repair damaged surfaces is a novel and particuraly desirable

characteristic of the invention.

The delivery/method of the alkali metal polyoxolates (or mineralization layer) can be

provided through a membrane from a reservoir as described in the U.S. Patent Application Serial

No. 08/634,215; previously incorporated by reference.   In the present invention, soluble

15   precursors, such as silicate materials, are used within one or more coating layers. For example,

in a polymer containing carrier system, one of the layers would be charged with sodium or

potassium silicates wherein the outer layer(s) are employed to control the rate of moisture flow

through the carrier. These carriers are typically relatively hard films as the normal

polymerization of the carrier occurs to form a plastic type polymer type coating. Additional

20   delivery methods have been developed utilizing soft films, gels, sealants, adhesives, and paints

wherein the membrane feature is formed in-situ by the reaction between a silicate, e.g., sodium

silicate, and silica. By controlling the quantity of the silica in the carrier, the mineralized layer

can be designed to suit the specific application. Depending upon the pH and relative

concentration of silicate and silica, the degree of crystal formation, e.g., a silica containing

25   hemimorphite within an amorphous layer, can also be designed to achieve a predetermined

result.

Without wishing to be bound by any theory or explanation the formation of the mineralized

layer can occur under a wide range of conditions (normally ambient) and via a plurality of

mechanisms. Normally, the mineralization layer forms underneath the carrier upon the metal

30   surface, e.g., as buried layer under a carrier comprising a reservoir of precursors. If so formed,

whatever ions are needed in the reservoir layer to form the mineralized layer, are expediently

included as water soluble salts in the reservoir layer. On the other hand, all the ions employed to

form the mineralized layer need not necessarily be included in the reservoir layer. That is, if

desired cations can be supplied from the underlying metal surface and need not necessarily be

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5   included as water soluble salts in the reservoir layer. Such cations can be obtained from the surface of the substrate metal itself, by reaction of the substrate with the anions of the precursor component for the mineralized layer. Since the mineralized layer is normally relatively thin, sufficient cations for the mineralized layer can even be supplied from the substrate when present only as an alloying ingredient, or perhaps even as an impurity. Additionally, the cations needed for the mineralized

10   layer can be supplied from water soluble salts in the reservoir layer, as indicated above. Further, if the mineralized layer is to be formed from an overlying reservoir layer that also contains buffer components, at least some to the salts used for buffering can be employed for forming the mineralized layer. The latter reservoir layer would possess a self healing effect by functioning as a source of minerization precursors in the event the layer was damaged. Once the mineralization

15   layer has been formed to the degree desired, the carrier or reservoir layer can remain as a component of the finished article or removed.

In one embodiment of the invention, silicon can provide the predominate lattice-forming unit, e.g., CRN. The fundamental unit on which the structure of all silicates is based on consists of four O^{2-} at the apices of a regular tetrahedron surrounding and coordinated by one Si^{4+} at the center.

20   A bond between silicon and oxygen atoms may be estimated by use of Pauling's electronegativity concept as 50% ionic and 50% covalent. That is, although the bond typically arises in part from the attraction of oppositely charged ions, the silicon-oxygen bond also involves sharing of electrons and interpretation of the electronic clouds of the ions involved. Each O^{2-} has the potential of bonding to another silicon atom and entering into another tetrahedral grouping, thus uniting the

25   tetrahedral groups through the shared (or bridging) oxygen. Such linking of tetrahedra is often referred to as polymerization. In the case of silicate polymerization, the amount of oxygen is normally less that the stoicheometric amount of 4:1, Si:O. Silicates in which two SiO_4 groups are linked can produce Si_2O_7 groups which are classed as disilicates. If more than two tetrahedra are linked, a closed ring like structure can be formed of a general composition Si_xO_{3x}. Fourfold

30   tetrahedral rings have composition Si_4O_{12}. Tetrahedra may also be joined to form infinite single chains, called pyroxenes with a unit composition of SiO_3. Infinite double chains, classified as amphibles, normally possess a ratio of Si:O = 4:11. Infinitely extending flat sheets are formed of unit composition Si_2O_5. Three dimensional framework silicates, such as feldspars or zeolites, typically result in a network oxide of unit composition SiO_2.

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5   In the present invention, silicates can be polymerized into a wide range of Si:O ratios. In the case of a zinc containing surface, the surface can interact with a mineral layer precursor to form a disilicate. In the case of an iron containing surface, the surface can interact with a suitable mineral layer precursor to form a chain silicate, e.g., a clinoperoxine. When silicate polymerization occurs in the instant invention, the covalency of the silicon-oxygen bond is decreased. This is

10   evidenced by an increased binding energy of the photoelecton as detected by x-ray photoelectron spectrospopy, e.g, a binding energy between 102.0 to 103.3 eV in comparison to 101.5 eV for orthosilicate.

        Without wishing to be bound by any theory of explanation it is also believed that the aforementioned inventive mineralized can comprise a complex oxide of the form:

15        $M_xN_yO_t$, wherein "M" represents one or more cationic elements having a covalency factor of less than about 0.5 that functions to balance the charge of the complex oxide, "N" represents one or more lattice forming elements having a covalency factor greater than about 0.15 that functions as the structural component of the complex oxide and optionally wherein the N_yO_t carries single or multiple crystal structures; and wherein x, y and t comprise any number the

20   total of which balances the charge of the complex oxide. In some cases, the covalency factor of M is less than about 0.33 and the covalency factor N is greater than about 0.33.

        Applications for the films and coatings of the invention include, for example, components such as coatings and paints of components, parts and panels for use the automotive industry, home-consumer products, construction and infrastructures, aerospace industry, and other out-door or

25   corrosive applications wherein it is desirable to improve the characteristics of a metal surface and the use of heavy metals in elemental or non-elemental form is environmentally undesirable. The films and coatings may be applied to new products or over conventional platings to extend the useful service life of the plated component.

        While the above description places particular emphasis upon forming a silicate containing

30   mineralized layer, one or more mineralized layers having chemically similar or distinct compositions can be applied upon the same metal surface. If desired, the mineralized surface can be further modified by using conventional physical or chemical treatment methods.

        The following Examples are provided to illustrate not limit the scope of the invention as defined in the appended claims. These Examples contain results of the following analysis: Auger

5   Electron Spectroscopy (AES), Electronic Impedance Spectroscopy (EIS), and Electron
        Spectroscopy for Chemical Analysis (ESCA) and Potentiodynamic (DC) Polarization. These
        analysis were performed using conventional testing procedures.   The results of the AES
        demonstrate that the thickness of the mineralized layer can range from about 10 to 50 microns. EIS
        demonstrates that the mineralized layer imparts corrosion resistant properties to the surface, e.g., a

10   reduced Icorr corresponds to a reduced corrosion current and in turn a reduced corrosion rate. The
        XPS data demonstrates the presence of a unique hemimorphite crystal within the mineralized layer,
        e.g., XPS measures the bond energy between silicon and oxygen atoms and compares the measured
        energy to standardized values in order to determine whether or not known crystals are present.
        Conventional X-ray diffraction analysis confirmed that the mineralized layer is predominately

15   amorphous, e.g., an X-ray measurement resulted in wide bands thereby indicating the presence of
        an amorphous phase.

                                        EXAMPLES
                                -Auger Electron Spectroscopy-
                Examples 1-4 were prepared and analyzed in accordance with the following AES

20   procedure.

        Instrumentation Used

        Instrument: Physical Electronics 545, Single Pass Cylindrical Analyzer
25   Sample Excitation: Electron Gun
                                        Emission Current, 1 mA
                                        Beam Voltage, 3 kV
        Electron Beam Detection: Multiplier Voltage, 1 kV
                                        Modulation Voltage, 3 eV
30   Signal Detection: Lock-in Magnification, 10X
                                        Lock-in Time Constant, 0.001 sec.
        Sputter Gun Settings: Beam Voltage, 3kV
                                        Focus Dial Setting, 2

                                            20

5   Raster X Dial Setting, 10

           Raster Y Dial Setting, 10

           Emission Current, 15, mA

           Sputter Rate, 12 Å/min

           Start Time, 0 min.

10   Final Time, 30 min

           Sputter Depth, 360 Å

Example 1

The coating had a first layer with the following formulation (by weight):

15

25% Water (Fisher Scientific)

75% NeoRezR-9637 (Zeneca Resins)

and a second layer with the following formulation (by weight):

20

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

25   The components were mixed by hand for approximately 15 minutes. The first layer was then

      cast onto a standard 1010 steel test panel, obtained through ACT Laboratories, with a dry film

      thickness of about 0.5 to 0.7 mil. This layer was dried to tack free at 60 C for 10 minutes. The

      second layer was then applied, with a dry film thickness of about 0.5 to 0.7 mil. This layer was

      also dried to tack free at 60 C for 10 minutes. The second layer was left on the panel for a

30   minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart

      Stores) and a plastic spatula. The residual coating was washed off with copious amounts of

      Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

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Example 2

The coating had one layer with the following formulation (by weight):

25% Water (Fisher Scientific)

75% NeoRezR-9637 (Zeneca Resins)

and a second layer with the following formulation (by weight)

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

The components were mixed by hand for approximately 15 minutes. The first layer was then cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, with a dry film thickness of about 0.5 to 0.7 mil. This layer was dried to tack free at 60 C for 10 minutes. The second layer was then applied, with a dry film thickness of about 0.5 to 0.7 mil. This layer was also dried to tack free at 60 C for 10 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual coating was washed off with copious amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

Example 3

The coating had one layer with the following formulation (by weight):

25% Water (Fisher Scientific)

75% NeoRezR-9637 (Zeneca Resins)

and a second layer with the following formulation (by weight)

5   6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

The components were mixed by hand for approximately 15 minutes. The first layer was then

10   cast onto a standard zinc phosphated, 1010 steel test panel, obtained through ACT Laboratories,

with a dry film thickness of about 0.5 to 0.7 mil. This layer was dried to tack free at 60 C for 10

minutes. The second layer was then applied, with a dry film thickness of about 0.5 to 0.7 mil.

This layer was also dried to tack free at 60 C for 10 minutes. The coating was left on the panel

for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart

15   Stores) and a plastic spatula. The residual was washed off with copious amounts of Naptha

(Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

Example 4

The coating had one layer with the following formulation (by weight):

20

25% Water (Fisher Scientific)

75% NeoRezR-9637 (Zeneca Resins)

and a second layer with the following formulation (by weight)

25

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

30   The components were mixed by hand for approximately 15 minutes. The first layer was then

cast onto a standard iron phosphated, 1010 steel test panel, obtained through ACT Laboratories,

with a dry film thickness of about 0.5 to 0.7 mil. This layer was dried to tack free at 60 C for 10

minutes. The second layer was then applied, with a dry film thickness of about 0.5 to 0.7 mil.

This layer was also dried to tack free at 60 C for 10 minutes. The coating was left on the panel

23

5   for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart

Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha

(Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

Each of the previously described washed test panels were passed through an AES

analysis in accordance with conventional methods. This analysis confirmed the presence of the

10   inventive mineral layer and generated data which demonstrated that for each substrate, the

thickness of the mineralized layer was on the order of about 50 to about 70 Å thick.

-Electrical Impedance Spectroscopy-

Examples 5 through 13 were prepared for Electrochemical Impedance Spectroscopy

15   (EIS) analysis. EIS is one method of determining corrosion rates of a metal or a coated metal. In

this technique, a small-amplitude sinusoidal potential perturbation was applied to the working

electrode at a number of discrete frequencies ranging from 60,000 Hz to 0.0005 Hz. At each one

of these frequencies, the resulting current waveform exhibited a sinusoidal response that was out

of phase with the applied potential signal by a certain amount. The electrochemical impedance

20   was a frequency-dependent proportionality factor that acts as a transfer function by establishing a

relationship between the excitation voltage signal and the current response of the system. This

method was detailed by the American Society for Testing and Materials (ASTM) in

Electrochemical Corrosion Testing, STP 727.

25   Example 5

A gel was prepared having the following formulation (by weight):

10% Cab-O-Sil TS-720 Silica

90% Amoco DURASYN™ 174 polyalphaolefin

30

The above formulation was mixed in a Hobart Mixer (model N-50) for approximately 30

minutes. The gel was then cast onto a standard electrogalvanized test panel, obtained through

ACT Laboratories, at a thickness of 1/16" to 1/8". The gel was left on the panel for a minimum

of 24 hours. Most of the gel was then removed with a plastic spatula. The residual gel was

24

5   washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent

Alcohol (Fisher Scientific).

Example 6

A gel was prepared having the following formulation (by weight):

10

10% Cab-O-Sil TS-720 Silica

20% G-Grade Sodium Silicate (PQ Corporation)

70% Amoco DURASYN™ 174 polyalphaolefin

15   The above formulation was mixed in a Hobart Mixer (model N-50) for approximately 30

minutes. The gel was then cast onto a standard electrogalvanized test panel, obtained through

ACT Laboratories, at a thickness of 1/16" to 1/8". The gel was left on the panel for a minimum

of 24 hours. Most of the gel was then removed with a plastic spatula. The residual was washed

off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol

20   (Fisher Scientific).

Example 7

A gel was prepared having the following formulation (by weight):

25   10% Cab-O-Sil TS-720 Silica

20% Sodium Molybdate (Fisher Scientific)

70% Amoco DURASYN™ 174 polyalphaolefin

The above formulation was mixed in a Hobart Mixer (model N-50) for approximately 30

30   minutes. The gel was then cast onto a standard electrogalvanized test panel, obtained through

ACT Laboratories, at a thickness of 1/16" to 1/8". The gel was left on the panel for a minimum

of 24 hours. Most of the gel was then removed with a plastic spatula. The residual was washed

off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol

(Fisher Scientific).

5

Example 8

A gel was prepared having the following formulation (by weight):

10% Cab-O-Sil TS-720 Silica

10   20% Sodium Phosphate (Fisher Scientific)

70% Amoco DURASYN™ 174 polyalphaolefin

The above formulation was mixed in a Hobart Mixer (model N-50) for approximately 30

minutes. The gel was then cast onto a standard electrogalvanized test panel, obtained through

15   ACT Laboratories, at a thickness of 1/16" to 1/8". The gel was left on the panel for a minimum

of 24 hours. Most of the gel was then removed with a plastic spatula. The residual was washed

off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol

(Fisher Scientific).

         This Example was repeated with the exception that sodium carbonate was employed

20   instead of sodium phosphate.

Example 9

A coating was prepared having the following formulation (by weight):

25   25% Water (Fisher Scientific)

75% NeoRezR-9637 (Zeneca Resins)

The above formulation was mixed by hand for approximately 15 minutes. The coating was then

cast onto a standard 1010 steel test panel, obtained through ACT Laboratories, at a thickness for

30   a total dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60

C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the

coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The

residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores),

and Reagent Alcohol (Fisher Scientific).

26

5

Example 10

A coating was prepared having the following formulation (by weight):

6.5% N-grade Sodium Silicate

10   13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

The above formulation was mixed by hand for approximately 15 minutes. The coating was then cast onto a standard 1010 steel test panel, obtained through ACT Laboratories, at a thickness for

15   a total dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

20

Example 11

A coating was prepared having the following formulation (by weight):

6.5% Sodium Vanadate Solution (156.3 grams/liter)

25   13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

The above formulation was mixed by hand for approximately 15 minutes. The coating was then cast onto a standard 1010 steel test panel, obtained through ACT Laboratories, at a thickness for

30   a total dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

27

5

Example 12

A coating was prepared having the following formulation (by weight):

10   6.5% Sodium Molybdate Solution (274.21 grams/ liter)

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

The above formulation was mixed by hand for approximately 15 minutes. The coating was then cast onto a standard 1010 steel test panel, obtained through ACT Laboratories, at a thickness for

15   a total dry film thickness of 2.1 to 2.5 mils in three layers. Each coat was dried to tack free at 60 C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

20

Example 13

A coating was prepared having the following formulation (by weight):

25   6.5% Sodium Carbonate Solution (120.12 grams/ liter)

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

The above formulation was mixed by hand for approximately 15 minutes. The coating was then

30   cast onto a standard 1010 steel test panel, obtained through ACT Laboratories, at a thickness for a total dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores),

5   and Reagent Alcohol (Fisher Scientific).

The cleaned samples from Examples 5 to 13 were then tested by EIS in accordance with the following method.

10   Instrument: Solartron 1287 Electrochemical Interface

Solartron 1260 Impedance/Gain-Phase Analyzer

ZWare and CorrWarr Software by Scribner

Settings: 60,000 to .005 Hz.

10 steps/decade

15   5 mV rms AC signal

Test Solution: 1Molar Ammonium Sulfate, pH = 3.0 (using 0.1 N Sulfuric Acid) for electrogalvanized substrates.

1Molar Ammonium Sulfate, pH = 2.0 (using 0.1 N Sulfuric Acid) for 1010 Steel substrates.

20   B value: corresponds to the average of the Tafel slope B = (BcBa)/(Bc + Ba)

icorr: corresponds to the current generated by corrosion

The following Table sets forth the results of the EIS Procedure for the zinc substrate in Examples 5-8.

25

EIS TABLE FOR ZINC SUBSTRATES

surface	B	i_{corr} $\mu A/cm^2$	ave. B	ave. i_{corr} $\mu A/cm^2$	EXPL NO.	Comments
Bare Zinc	0.062632	193.3	0.067255	205.5	standard	
	0.060229	204.4			std	
	0.063586	226.3			std	
	0.101038	85.3			std	1

[1] Cell leaked at the base, setting up a localized galvanic cell.

	0.071548	213.1			std	
	0.0792307	243.6			std	
	0.078282	190.2			std	
Gel	0.054997	120.4	0.055658	130.1	5	
	0.045513	148.5			5	
	0.035642	64.8			5	
	0.041034	79.7			5	
	0.039146	72.5			5	
	0.060190	113.1			5	
	0.061932	138.5			5	
Na_2SiO_4	0.072070	110.7	0.047529	97.5	6	
	0.059899	121.5			6	
	0.035932	93.2			6	
	0.038235	107.7			6	
	0.040076	67.3			6	
	0.038964	84.7			6	

---

[1] Cell leaked underneath gasket.

5

ZINC EIS TABLE CONTINUED

surface	B (mV)	i_{corr} µA/cm²	ave. B (mV)	ave. i_{corr} µA/cm²	EXMPL NO	Comments
Na_2MoO_4	0.052667	99.3	0.061923	128.5	7	
	0.072482	191.1			7	
	0.059900	98.5			7	
	0.065942	128.6			7	
	0.058622	125.0			7	
	0.090991	153.9			7	[2]
Na_2PO_4	0.047173	93.3	0.049479	153.9	8	
	0.045828	141.0			8	
	0.053326	232.8			8	
	0.056754	178.1			8	
	0.058574	194.0			8	
	0.035220	84.2			8	
Na_2CO_3	0.041397	68.4	0.047339	98.7	8	
	0.044320	121.8			8	[2]
	0.046295	81.1			8	
	0.057343	123.4			8	[3]

The results of the EIS indicates that the greatest corrosion resistance (low icorr) for a zinc

10   substrate is obtained by a sodium silicate or sodium carbonate mineral layers.

The following Tables list the corrosion data for the steel surfaces of Examples 9-13.

---

[2] Cell leaked at the base, discarded this data point.

	44	31.5	125	252
-	68	33.8	172	196, pH = 2.25
steel - coating was not completely stripped	1	36.7	564	65
steel	26	33.2	371	90
-	57	33.2	554	60
steel - coating was restripped	1	42.4	32.6	1300
steel	1	42.2	59.7	707
-	24	40.8	58.7	695
-	48	40.8	70.2	581, pH = 2

5

Coating Containing Sodium Vandate - Example 11

surface	Hours Immersed	B (mV)	R_p (ohm-cm^2)	i_{corr} (μA/cm^2)
steel	25	305.8	55.5	645
-	49	33.9	75.8	448
-	74	33.9	82.6	410, pH = 2.8
-	78	42.2	25.7	1640, pH = 2
-	1.5	50.5	70	721
-	21	36.5	92	397
-	44	33.3	126	265
-	68	33.2	161	206, pH = 2.25
-	1	40.8	146	280
-	24	40.6	64.6	632
-	48	40.6	75.6	537, pH = 2

5

Coating Without Silicates-Example 9

surface	Hours Immersed	B (mV)	R_p (ohm-cm^2)	i_{corr} (μA/cm^2)
steel	24	39.4	68	580
-	49	33.8	55	614
-	74	33.8	116	290, pH = 2.86
-	99	33.8	25	1352, pH = 2.0
-	21	34.4	54	637
-	44	36.3	95.8	379
-	68	45	55.6	808, pH = 2.36
-	1	46.1	59.3	777
-	24	41.7	43.8	952
-	48	43.3	55.5	780, pH = 2.4
-	1	42	135	311
-	24.5	40.8	51.8	788
-	48	40.5	53	764, pH = 2.5

Coating Containing Sodium Silicate-Example 10

surface	Hours Immersed	B (mV)	R_p (ohm-cm^2)	i_{corr} (μA/cm^2)
steel	24	30.3	47.5	640
-	49	35.3	55	642
-	74	35.3	267	132, pH = 3.15
-	99	35.3	20	1765, pH = 2
-	1.5	43.4	74.4	584
-	21	35.5	94.2	377

surface	Hours Immersed	B (mV)	R_p (ohm-cm^2)	i_{corr} (μA/cm^2)
-	1	42.6	62.9	677
-	24	34.6	65	536
-	48	39.1	110	355, pH = 2.1

Coating Containing Sodium Molybdate - Example 12

surface	Hours Immersed	B (mV)	R_p (ohm-cm^2)	i_{corr} (μA/cm^2)
steel	21	37.4	51.3	729
-	44	44.4	45.6	973
-	68	41.4	54.3	763, pH = 2.35
steel - coating was not completely removed	1	37.7	190	198
steel	26	36.6	138	265
-	57	36.6	212	173
steel - coating was not completely removed)	1	33.3	112	353
-	24	40.4	96.6	409
-	48	39.5	130	293, pH = 2.2
-	1	46.9	42.5	1109
-	24	48.2	28.6	1687
-	44	46	45.2	1018, pH = 2.15

Coating Containing Sodium Carbonate - Example 13

34

surface	Hours Immersed	B (mV)	R_p (ohm-cm^2)	i_{corr} ($\mu A/cm^2$)
steel	25	37.2	82.5	451
-	49	27.6	123.5	223
-	74	27.6	128.8	214, pH = 2.3
-	78	37.2	34.4	1080, pH = 2
-	1	41.8	56.8	735
-	24.5	44.2	33.5	1320
-	48	43.4	40.7	1066, pH = 2.9
-	1	39.5	112	353
-	24	40.6	96.6	409
-	48	38.1	130	293, pH = 2.2
-	1	45.7	46.7	978
-	24	46.5	29.7	1566
-	44	44.4	41.4	1072 pH = 2.15

Based upon the measured corrosion currents, sodium carbonate and sodium silicate are the most effective in reducing the icorr thereby indicating a reduced corrosion rate.

- X-Ray Photoelectron Spectroscopy (XPS) -

X-ray Photoelectron Spectroscopy (XPS) was performed on a series of samples in Examples 14-24 that included 1010 Steel and Electrogalvanized Steel. XPS was performed in accordance with conventional procedures in this art.

Instrumentation Used

Instrument: Physical Electronics 5701 LSci

X-ray Source: Monochromatic aluminum

Source Power: 350 watts

Analysis Region: 2 mm X 0.8 mm

Exit angle: 65°

35

5   Acceptance angle: ±7°

       Charge reference: B.E. of C-)H,C) = 284.6 eV

       Charge neutralization: flood gun

       Sampling Depth: (3λ) was 70 Å

10

Example 14

A coating was prepared having the following formulation (by weight):

       25% Water (Fisher Scientific)

15   75% NeoRezR-9637 (Zeneca Resins)

       The above formulation was mixed by hand for approximately 15 minutes. The coating was then

       cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total

       dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for

20   15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating

       was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was

       washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent

       Alcohol (Fisher Scientific).

25   ## Example 15

A coating was prepared having the following formulation (by weight):

       25% Water (Fisher Scientific)

       75% NeoRezR-9637 (Zeneca Resins)

30   The above formulation was mixed by hand for approximately 15 minutes. The coating was then

       cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total

       dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for

       15 minutes. The coated panel was then exposed to a post-cure heat treatment of 1 hour at 125° C,

       using a standard laboratory oven. The coating was left on the panel for a minimum of 24 hours.

5   Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

Example 16

10   A coating was prepared having the following formulation (by weight):

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

15

The above formulation was mixed by hand for approximately 15 minutes. The coating was then cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating

20   was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent Alcohol (Fisher Scientific).

Example 17

25   A coating was prepared having the following formulation (by weight):

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

30

The above formulation was mixed by hand for approximately 15 minutes. The coating was then cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for 15 minutes. The coating was left on the panel for a minimum of 24 hours. Most of the coating

5   was then removed with BIX Stripper (Walmart Stores) and a plastic spatula. The residual was
     washed off with copius amounts of Naptha (Commercial Grade, Walmart Stores), and Reagent
     Alcohol (Fisher Scientific).

Example 18

10   A coating was prepared having the following formulation (by weight):

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

15

The above formulation was mixed by hand for approximately 15 minutes. The coating was then
cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total
dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for
15 minutes. The coated panel was then exposed to a post-cure heat treatment of 125° C for one

20   hour, in a standard laboratory oven. The coating was left on the panel for a minimum of 24
     hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic
     spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade,
     Walmart Stores), and Reagent Alcohol (Fisher Scientific).

Example 19

25   A coating was prepared having the following formulation (by weight):

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

30   80.5% NeoRezR-9637 (Zeneca Resins)

The above formulation was mixed by hand for approximately 15 minutes. The coating was then
cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total
dry film thickness of 2.1 to 2.5 mils in three layers. Each layer was dried to tack free at 60 C for

5   15 minutes. The coated panel was then exposed to a post-cure heat treatment of 175° C for one

hour, in a standard laboratory oven. The coating was left on the panel for a minimum of 24

hours. Most of the coating was then removed with BIX Stripper (Walmart Stores) and a plastic

spatula. The residual was washed off with copius amounts of Naptha (Commercial Grade,

Walmart Stores), and Reagent Alcohol (Fisher Scientific).

10

Example 20

For purposes of comparing the results achieved by Examples 14-19, an electrogalvanized

panel was soaked for 24 hours in a solution that had the following formulation (by weight):

15   25 mg/l Sodium Silicate

The sample panel was allowed to air dry.

Example 21

20   For purposes of comparing the results achieved by Examples 14-19, an electrogalvanized

panel was soaked for 24 hours in a solution that had the following formulation (by weight):

25 mg/l Sodium Silicate

25   The sample panel was allowed to air dry. The panel was then exposed to a post-dry heat

treatment of 125° C for one hour, in a standard laboratory oven.

Example 22

For purposes of comparing the results achieved by Examples 14-19, an electrogalvanized

30   panel was soaked for 24 hours in a solution that had the following formulation (by weight):

25 mg/l Sodium Silicate

39

5   The sample panel was allowed to air dry. The panel was then exposed to a post-dry heat

treatment of 175° C for one hour, in a standard laboratory oven.

Example 23

A crystal sample of Zn_2SiO_4, which was air fractured and immediately introduced into the

10   sample chamber of the XPS. The total air exposure was less than 2 minutes. The surface was

examined initially with a low resolution survey scan to determine which elements were present.

High resolution XPS spectra were taken to determine the binding energy of the elements detected

in the survey scan. The quantification of the elements was accomplished by using the atomic

sensitivity factors for a Physical Electronics 5701 LSci ESCA spectrometer.

15   The following Table sets forth the silicon binding energies which were measured for

Examples 14-23.

Example Number	Treatment	Si 2p peak Energy (eV)
14	Room Temp	101.9
15	125 °C	101.8
16	Room Temp	102.8
17	Room Temp	102.8
18	125 °C	102.6
19	175 °C	102.6
20	25 ppm Na_2SiO_4, 25 °C	101.7
21	25 ppm Na_2SiO_4, 125 °C	101.7
22	25 ppm Na_2SiO_4, 175 °C	101.8
23	Zn_2SiO_4 crystal	101.5

The above Table illustrates that there has been a change in the concentration of Si as well

40

5   as the bond energy thereby providing further confirmation of the presence of the mineralized

layer. Further, the Si-O bond energy of conventional zinc silicate crystal as well as the silicate

soaked panels is distinct from the inventive mineralized layer.

Example 24

10   A coating was prepared having the following formulation (by weight):

6.5% N-grade Sodium Silicate

13% Water (Fisher Scientific)

80.5% NeoRezR-9637 (Zeneca Resins)

15

The formulation above was mixed by hand for approximately 15 minutes. The coating was then

cast onto a standard electrogalvanized test panel, obtained through ACT Laboratories, for a total

dry film thickness of 2.1 to 2.5 mils in three coats. Each coat was dried to tack free at 60 C for

15 minutes. The panel was exposed to ASTM B117 Salt Fog Chamber for 2400 hours. At the

20   end of the salt fog exposure, there were large areas of the panel that were uncorroded. The area

of uncorroded surface was cut into a small square sample and the urethane coating was removed

by hand, using small tweezers. The sample was analyzed in accordance with the previously

identified XPS method on an instrument of comparable sensitivity and accuracy. The results of

the XPS are set forth in the following Table.

25

Example 24 Silicate Containing Coating Followed by Salt Spray Exposure

Example Number	Treatment	Si 2p peak Energy (eV)	Relative Concentration of Silicon on the Surface (% wt)
14	urethane coating, room temp	101.9	negligible at 1.0 %
15	urethane coating, 125 °C	101.8	negligible at 0.8 %

16	silicate, room temp	102.8	19.8 %
17	silicate 125 °C	102.8	18.9 %
18	silicate, room temp	102.6	15.8 %
19	silicate, 175 °C (heat applied after coating removed)	102.6	11.6 %
20	immersion, 25 ppm Na_2SiO_4, 25 °C	101.7	4.1 %
21	immersion, 25 ppm Na_2SiO_4, 125 °C	101.7	3.2 %
22	immersion, 25 ppm Na_2SiO_4, 175 °C	101.8	3.9 %
23	Zn_2SiO_4 crystal	101.5	NA
24	silicate, room temp, 2400 hours of B117 exposure	102.6	8.1 %

The above Table illustrates that the binding energy for the surface exposed to the silicate containing coatings range from 102.6 to 102.8. By observation of the XPS peak, it was observed that these energy values were actually manifold values from manifold peaks that contain more than one material. These materials can be characterized as a disilicate, or hemimorphite (bonding energy at 102.2), altered by the presence of Si-O bonds, as in SiO2 (bonding energy at 103.3) and Si-O-C bonds with a bonding energy of 103.6 or 103.7. Such a bonding energy and

42

5   concentration of Si on the surface are distinct from conventional silica or silicate structures. The

binding energy, for zinc silicate, Zn_2SiO_4,101.5 eV, is also distinct from the binding energy of

the mineralized layer, 102.7 eV, or the hemimorphite.

EXAMPLE 25

10   This Example illustrates a process for pretreating a metal surface in order to enhance

formation of the inventive silicate containing layer/surface.

1. Immerse panel in solution of 25% Metalprep 79 (Parker-Amchem) for 2 minutes,

2. Remove Panel and rinse with deionized water,

15   3. Scrub panel gently with "Kim-Wipe",

4. Rinse with deionized water and wipe off excess with Kim-wipe,

5. Immerse panel in 0.1 M NaOH solution for 10 sec.,

6. Wipe off excess with Kim-wipe,

7. Immerse panel in 50% H2O2 solution for 5 min.; and,

20   8. Wipe off excess with Kim-wipe.

EXAMPLE 26

A cold rolled steel panel (ACT Labs) was prepared with the pretreatment process

described in Example 25. The pretreated panel was then coated with a first layer comprising the

25   following formulation (by wt%):

25% Water (Fisher Scientific); and,

75% NeoRezR-9637 (Zeneca Resins).

30   A second and third layer comprising the following formulation were then applied upon

the first layer (by weight):

13% N-grade Sodium Silicate,

43

5   6.5% Water (Fisher Scientific); and,

       80.5% NeoRezR-9637 (Zeneca Resins).

       Each aforementioned formulation was mixed by hand for approximately 10 minutes.

Each layer was applied at a 1.2 mil wet film thickness and cured for 15 minutes at 60 C to form

10   for a tack-free finish. The panels were allowed to set overnight (or longer) and the coating was

physically removed by hand.

       XPS analysis was performed on the surface of this panel. The characteristic NaFe

$(SiO_3)_2Si(2p)$ photoelectron binding energy was used to identify the species on the surface. The

surface was characterized as a iron pyroxene species with the empirical formula of $NaFe(SiO_3)2$.

15   Comparison of a clinopyroxene, a naturally occurring iron pyroxene, indicates that the species

on the surface of the panel is indeed a matrix of a polymerized SiO_3 and iron.

                                    EXAMPLE 27

       A electrozinc galvanized panel (ACT Labs) was prepared with the pretreatment method

20   described above in Example 25. The panel was then coated with the following first formula (by

wt%):

       25% Water (Fisher Scientific); and,

       75% NeoRezR-9637 (Zeneca Resins).

25

       A second and third layer with the following formulation (by weight) were applied upon

the first layer:

       6.5% N-grade Sodium Silicate,

30   13% Water (Fisher Scientific); and,

       80.5% NeoRezR-9637 (Zeneca Resins).

Each formula was mixed by hand for approximately 10 minutes. Each layer was applied at a 1.2

mil wet film thickness and given a 15 minute 60 C cure to allow for a tack-free finish. The

                                         44

5   panels were allowed to set for 1 hour and the coating was physically removed by hand.

EXAMPLE 28

A electrozinc galvanized panel (ACT Labs) was prepared with the pretreatment method

described in Example 25. The panel was then coated with two layers of the following formula

10   (by wt%):

1.0% N-grade Sodium Silicate,

18.5% Water (Fisher Scientific); and,

80.5% NeoRezR-9637 (Zeneca Resins).

15

Each formula was mixed by hand for approximately 10 minutes. Each layer was applied at a 1.2

mil wet film thickness and given a 15 minute 60 C cure to allow for a tack-free finish. The

panels were allowed to set for 24 hours and the coating was physically removed by hand.

The coated galvanized panels were recovered and analyzed in accordance with the

20   previously described ESCA/XPS methods. XPS analysis was performed on both panels. A first

panel shows the Si(2p) photoelectron binding energy of 102.1 eV representing a zinc disilicate

species. A second panel also shows the same binding energy at 102.1 eV also indicating the

presence of a zinc disilicate species on the surface of the zinc. The second test panel also has

significantly more silica on the surface, represented by the 103.3 eV binding energy than does

25   the first panel. Because of the accumulation of silica on the surface of panel #2, the relative

amount of zinc decreases due to the limited sampling depth of XPS. The Zn:Si ratio goes down

from 2.0 to 0.43 on panel #1 to panel #2, respectively, as would be expected when the build up of

silica increases on the panel surface. In both cases, the formation of a zinc disilicate protective

species was detected.

30

EXAMPLE 29

Cold rolled steel panels (ACT Laboratories) were coated with the following formula (by

wt%) to form a first layer:

45

5   25% Water (Fisher Scientific); and,

75% NeoRezR-9637 (Zeneca Resins).

A second layer with the following formulation (by wt%) was applied upon the first layer:

10

X% N-grade Sodium Silicate,

(19.5-X)% Water (Fisher Scientific); and,

80.5% NeoRezR-9637 (Zeneca Resins),

15   wherein X is a number, either 1.0 or 0.01 wt.%, as described below. A second layer with the

same composition of the first layer was applied. Each formula was mixed by hand for

approximately 10 minutes. Each layer was applied at a 1.2 mil wet film thickness and given a 15

minute 60 C cure to allow for a tack-free finish. Each panel was given a heat treatment for 1

hour at the temperature described in the table below. The panels were allowed to set overnight .

20

Panel Set #	Silicate conc (X%)	Heat temp (C)	B2247 fail time Humidity	Adhesion rating
1	0.01	60	8	1
2	0.01	125	8	9
3	1.0	60	24	1
4	1.0	125	24	10

Two sets of tests were performed to examine the degree of protection against corrosion

and the adhesion properties of the urethane coating to the steel surface. Corrosion protection was

measured by time to reach 5% red rust coverage by humidity exposure according to ASTM

25   B2247. Adhesion was measured by immersing the panels in deionized water for 10 minutes

followed by 24 hour humidity exposure. The panel coatings were then scribed using a razor

blade in a "X" pattern. Tape was placed over the scribe and pulled back. Performance was rated

on a scale of 1-10, 1 = no adhesion and complete removal of coating, 10 = excellent adhesion, no

5   removal of coating.

The results, illustrated in the table above, show that increased loadings of silicate in the urethane coating improve corrosion protection. For best results, the amount of mineral layer precursor or sodium silicate is greater than 0 and less than about 7 wt.%, normally about 0.1 to about .01 wt/% silicate, and heat treated at a temperature of about 125 C.

10   It is to be understood that the foregoing is illustrative only and that other means and techniques may be employed without departing from the spirit or scope of the invention as defined in the following claims.

15

EXAMPLE 30

The corrosion resistance of the following formulations were evaluated by salt spray testing per ASTM-B117 specifications with the panels positioned with the 6 inch long edge at the top and the bottom to preclude each of the test areas on each panel from affecting the adjacent

20   area.

The coating formulations were prepared as follows:

1. Formula #1: was prepared by adding 781 g. water to 2342 g. NeoRez R9637 polyurethane
25   dispersion (Zeneca Resins) to achieve a composition of 75% by weight R9637 and 25% by weight water. The viscosity of the composition was 35 cP Brookfield (#2 spindle, speed 20, 70°F).

2. Formula #2: was prepared by diluting 143.5 mL N grade sodium silicate solution (PQ
30   Corporation) with 345 mL distilled water and slowly mixing this into 2134.5 grams of NeoRez R9637 resin while stirring with an air powered Jiffy Mixer for approximately 15 minutes. The viscosity of the composition was 38 cP Brookfield (#2 spindle, speed 20, 70°F) and had a pH of 10.5 (pH paper).

47

5

The coatings formulations were used to coat electrogalvanized steel panels and hot-dipped galvanized zinc panels. The electrogalvanized panels were supplied by ACT (ACT E60 EZG 60G) 2 side, clean, unpolished. The hot-dipped galvanized panels were obtained from a metal building supplier (Bulter) and cut to size specifications. Each coating layer was applied with a

10   #12 Jr. Drawdown rod to produce a 1.2 mil wet film coating thickness. Each coating layer was dried to a tack free condition by baking in a forced air convection oven at 60 C for 15 minutes before subsequent coating layers were applied. The overall dry film coating thickness on all of the panels averaged 1.4 mils.

15   **Sample 1:**

Sample Name: Egal Control Sample

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: None (control sample)

Additional Treatments: None

20

Sample 2:

Sample Name: Hot-dipped Control Sample

Substrate: HotDipped Zinc Panel 03X06X075

Coating: None

25   Additional Treatments: None

Sample 3:

Sample Name: Urethane Control Sample

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

30   Coating: 3 coats of Formula #1

Additional Treatments: None

Sample 4:

48

5   Sample Name: Heated Urethane Control Sample

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: 3 coats of Formula #1

Additional Treatments: 75°C for 1 hour

10   **Sample 5:**

Sample Name: Single Formula #2 Coat

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: 1 coat of Formula #2

Additional Treatments: None

15

Sample 6:

Sample Name: Single Formula #2 + Topcoat

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: 1 coat of Formula #2, than 1 coat of Formula #1

20   Additional Treatments: None

Sample 7:

Sample Name: 2-layers of Formula #2

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

25   Coating: 2 coats of Formula #2

Additional Treatments: None

Sample 8:

Sample Name: Single layer of Formula #2 + Topcoat

30   Substrate: HotDipped Zinc Panel

Coating: 1 coat of Formula #2, than 1 coat of Formula #1

Additional Treatments: None

49

5   **Sample 9:**

Sample Name: 3-layer Formula #2

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: 3 coats of Formula #2

Additional Treatments: None

10

Sample 10:

Sample Name: 3-layers of Formula #2

Substrate: HotDipped Zinc Panel.

Coating: 3 coats of Formula #2

15   Additional Treatments: None

Sample 11:

Sample Name: 2 layers of Formula #2 + Topcoat

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

20   Coating: 2 coat of Formula #2, than 1 coat of Formula #1

Additional Treatments: None

Sample 12:

Sample Name: 2 layers of Formula #2 + Topcoat

25   Substrate: HotDipped Zinc Panel.

Coating: 2 coat of Formula #2, than 1 coat of Formula #1

Additional Treatments: None

Sample 13:

30   Sample Name: 2 layers of Formula #2 + Topcoat + Heat

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: 2 coat of Formula #2, than 1 coat of Formula #1

Additional Treatments: 75° C for 1 hour

50

Sample 14:

Sample Name: 2 layers of Formula #2 + Topcoat + Heat

Substrate: ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panel.

Coating: 2 coat of Formula #2, than 1 coat of Formula #1

Additional Treatments: 175° C for 1 hour

The results of analyizing the above Samples in accordance with ASTM B117.

Sample No.	Substrate	Performance Hours ASTM B117 1st Red	5% Red Rust
1 Zinc Egalv Control		24	120
2 Zinc Hot-dipped Control		24	528
3 Urethane Control		320	452
4 Heated Urethane Control		384	672
5 Single Layer		864	1080
6 Single Layer + Topcoat		876	1100
7 2-Layer		1288	1476
8 Single Layer + Topcoat		1308	1500
9 3-Layer		1206	1320
10 3-Layer		1200	1300
11 2-Layer + Topcoat		1336	1608
12 2-Layer + Topcoat		2000	2400
13 2-Layer + Topcoat + Heat		2300+	2600+
14 2-Layer + Topcoat + Heat		2500+	3000+

The above Table illustrates that the instant invention can be employed for increasing the corrosion resistance of a zinc containing surface by a factor of at least 8, e.g, compare samples 4

5   and 14.

                                    Example 31

        This Example illustrates whether or not corrosion resistance is imparted by an alkaline

pH (attributed to Sodium Hydroxide) and whether the presence of the soluble silicate ion offers

10   any additional protection beyond the contribution of the alkaline pH.

        This Example was performed by preparing and testing three sets of formulations:

        1. 3 layers of polymer with no additives.

        2. 3 layers of water-borne polymer with a pH adjusted to that of a alkali silicate doped

15   coating.

        3. 3 layers of polymer with sodium silicate added.

The coating formulations were prepared as follows:

20   1. The coating for formulation 1. was prepared by adding 781 g. water to 2342 g.

                NeoRez R9637 polyurethane dispersion (Zeneca Resins) to achieve a composition of

                75% by weight R9637 and 25% by weight water. The viscosity of the composition

                was 35 cP Brookfield (#2 spindle, speed 20, 70°F).

25   2. The coating for formulation 2. was prepared by dissolving 2.4335g. NaOH (sodium

                hydroxide powder) in 41.2 G. of distilled water. This sodium hydroxide solution was

                slowly mixed into 254 g. NeoRez R9637 resin with an air powered Jiffy Mixer over

                the course of 5 minutes. The viscosity of the composition was 60 cP Brookfield (#2

                spindle, speed 20, 70°F) and had a pH of 10.5 (pH paper).

30

            3. The coating for formulation 3. was prepared by diluting 143.5 mL N grade sodium

                silicate solution (PQ Corporation) with 345 mL distilled water and slowly mixing this

                into 2134.5 grams of NeoRez R9637 resin while stirring with an air powered Jiffy

                Mixer for approximately 15 minutes. The viscosity of the composition was 38 cP

                                        52

5   Brookfield (#2 spindle, speed 20, 70°F) and had a pH of 10.5 (pH paper).

The coating formulations were used to coat electrogalvanized steel panels. The electrogalvanized panels were ACT E60 EZG 60G 2 side, clean, unpolished from APR 29396 Batch 30718614. Each coating layer was applied with a #12 Jr. Drawdown rod to produce a 1.2 mil wet film

10   coating thickness. Each coating layer was dried to a tack free condition by baking in a forced air convection oven at 60 C for 15 minutes before subsequent coating layers were applied. The overall dry film coating thickness on all of the panels averaged 1.4 mils. The following panels were prepared:

surface	First Layer	Second Layer	Third Layer	alkali
Egalv	Formula #1	Formula #1	Formula #1	PANTST27
Egalv	Formula #3	Formula #3	Formula #3	ConNaOH
Egalv	Formula #2	Formula #2	Formula #2	Zn-NaOH

15

Five panels each having the surface and layering shown in the above Table were subjected to ASTM-B117 salt spray exposure until all panels in the group developed red corrosion on 5% of its surface, or approximately 1500 hours of test exposure was achieved. The

20   average time in test hours to the development of first red corrosion and to development of red corrosion on 5% of each sample surface(Failure) is shown in the Table below:

AVERAGE SALT SPRAY RESULTS FOR ELECTROGALVANIZED STEEL PANELS

25

Coating Formulation	Avg Hours First Red	Avg Hours 5% Red (Fail)
Polyurethane Only	308	448

53

Polyurethane pH Adjusted	456	616
Polyurethane + Na Silicate	1176*	1336**

*Two test panels did not develop red corrosion during the ASTM B117 Test.

**Two test panels did not develop red corrosion during the ASTM B117 Test.

The above two Tables illustrate that when applied over electrogalvanized steel panels, polyurethane coatings which contain sodium silicate perform a minimum of three times better than the polyurethane coating by itself, whereas only a 1.5 times improvement can be obtained by adjusting the polyurethane coating pH to 10.5. The presence of the sodium silicate imparts a corrosion resistance benefit significantly greater than that arising from the alkaline pH.

Example 32

The purpose of this Example is to determine the effect on corrosion resistance of adding different loadings of G grade sodium silicate powder (PQ Corporation) to a urethane carrier.

The 1,5,10,15,20,25,30 wt.% sodium silicate batches were prepared by adding 2,10,20,30,40,50,and 60 grams, respectively, of G grade sodium silicate powder(PQ Corporation) to 200 grams of PAO Grease(AM940126 supplied by Nye Lubricants Inc.) and mixing by hand for approximately 30 minutes.

The mixed silicate containing grease was evaluated by applying the grease upon ACT E60 EZG 60G 2 Side E-Galv., clean, unpolish zinc coated panels. The grease was applied to the panels by applying an excess to the panels and running a gate type applicator across the panels to leave behind a 1/16 inch thick gel coating. Two panels were coated per substrate/grease loading.

Prior to testing, the grease was removed from the bottom 3-3.5 inches of the panels by lightly scraping the excess off with manilla tags, leaving a thin film of gel on the surface. The base oil of the gel was then removed from this thin film by soaking and rinsing with naphtha. The cleaned surface of the panels appeared to be covered with a thin white deposit postulated to be silica and sodium silicate. Each test panel consisted of an uncoated area approximately 1 inch wide at the hole end of the panel followed by a 1.5-2 inch width containing unremoved gel and finally containing a 3-3.5 inch wide area where the gel had been removed.

5   The panels were evaluated by salt spray testing per ASTM-B117 specifications with the
panels positioned with the 6 inch long edge at the top and the bottom to preclude each of the test
areas on each panel from affecting the adjacent area.

Wt% silica	test basis	Salt Spray Hours (ASTM B117)		
		Panel 1	Panel 2	Average hours
0	First Red	480	672	576
	5% Red	648	1224	936
1	First Red	504	816	660
	5% Red	792	1248	1020
5	First Red	1296	1320	1308
	5% Red	2064	1872	1968
10	First Red	1320	1368	1344
	5% Red	1584	1536	1560
15	First Red	1176	1176	1176
	5% Red	1416	1536	1476
20	First Red	768	1200	984

	5% Red	1080	1416	1248
25	First Red	1152	1200	1176
	5% Red	1416	1416	1416
30	First Red	1152	1200	1176
	5% Red	1320	1416	1368

The corrosion resistance of zinc coated panels was affected by the amount of silicate in the carrier. The above Table demonstrates that the presence of at least 1% sodium silicate significantly enhances the corrosion performance.

EXAMPLE 33

Electrozinc galvanized steel panels (ACT Laboratories) were coated with two layers of the following formula (by wt%)

X% N-grade Sodium Silicate,

(19.5-X)% Water (Fisher Scientific); and,

80.5% NeoRezR-9637 (Zeneca Resins),

wherein X is a number, either 1.0, 0.1, or 0.01, as described below in greater detail. A final layer with the same composition of the first layer was applied. Each formula was mixed by hand for approximately 10 minutes. Each layer was applied at a 1.2 mil wet film thickness and given a 15 minute 60 C cure to allow for a tack-free finish. The panels were allowed to set overnight.

Two sets of tests were performed on these panels to examine the degree of formation of a zinc disilicate protective species and the adhesion properties. XPS analysis was performed on the panels with the urethane layer removed. The Si(2p) photoelectron binding energy signature

56

5   of 102.1 eV representing the zinc disilicate protective species was examined to determine its

presence. Adhesion was measured by immersing the panels in deionized water for 10 minutes

followed by 24 hour humidty exposure. The panel coatings were then scribed using a razor blade

in a "X" pattern. Tape was placed over the scribe and pulled back. Performance was rated on a

scale of 1-10, 1= no adhesion and complete removal of coating, 10= excellent adhesion, no

10   removal of coating.

Panel Set #	Silicate conc (X%)	Formation of Zinc Disilicate	Adhesion rating
1	1.0	Yes	10
2	0.1	Yes	10
3	0.01	No	10

All panels show excellent adhesion of the urethane layer to the surface of the zinc

substrate. A silicate concentration of aoubt 0.01 wt% in the urethane formula used above does

15   not allow for the formation of zinc disiliicate on the surface of the zinc.

EXAMPLE 34

This Example illustrates the partial mineral formation on zinc galvanized surfaces. The

zinc surface was prepared under controlled conditions to capture the formation process at

20   different stages and was analyzed using ESCA, AFM, and salt spray exposure in order to

correlate formation to salt spray performance. Testing illustrated that there is a correlation

between hemimorphite formation and salt spray performance. The data also shows a possible

reaction pathway.

The purpose of this experiment was to control the formation of the zinc silicate species on

25   the surface. When the protective species possess the characteristic peak, the intensity should

correlate to the degree of corrosion protection. The intensity of the peak was affected by the

thickness of the zinc silicate formed and/or the percent coverage of the surface. Thicker coverage

prolonged corrosion protection however, incomplete coverage produced immediate failure. To

slow down the mineral layer formation rate on the surface, three techniques were employed. The

57

5   first was to lay down a "non-active" urethane coat (one without any silicate). When the active
    layer is applied, the silicate will then have a barrier of diffusion to migrate through slowing down
    the rate of reaction. The next technique was to apply active coatings with lower amounts of
    silicate done under the assumption the reaction rate is dependent upon this reactant. The last
    method was to remove the coating at different times, thus stopping the reaction at known times.

10   Electrozinc galvanized panels were obtained from ACT Laboratories (EZG 60G). Each
    panel was washed with reagent alcohol to remove any oils. The panels were coated based on the
    scheme showed below in table 1. The three factors being studied are the number of base coats (0
    or 1), the concentration of the silicate used in the urethane layer (1% or 6.5%), and time of
    coating removal (1 hr or 2 days). Each factor and the recipe matrix is shown in table 1. Each

15 panel will be coated with or without the base coat as called for by the experimental matrix. The
    panel was then be coated with two layers of the active coat using the specified concentration.
    Coating was done using a #12 draw down bar. Each coat was cured for 15 minutes at 60 C. The
    removal of the coating was done by applying an excessively thick coating of urethane. This was
    done to increase tensile strength of the coating to facilitate the easy removal of the coating.

20   The base resin used for all the coatings was NeoRez R9637 (Zeneca). Resin
    concentration was held at 80.5 wt%. The appropriate amount of N-grade sodium silicate solution
    (PQ) was diluted and slowly added into the resin while stirring. Concentrations of the silicate
    solutions before dilution were 0,1, or 6.5 wt%. The solution was then topped off with water.
            Samples were tested in accordance with the previously described ESCA analysis

25 techniques. The results of the ESCA testing are set forth in the following table.

30

Panel	Strategy	Si(2p)	Species	Zn:Si

4	0-2-0	103.2	silica	0.26
	48hrs, 6.5%			
3	0-2-0	102.0 (60%)	disilicate	(0.4±
	48hrs, 1%	103.1 (40%)	silica	0.1)
2	1-2-0	102.1 (83%)	disilicate	1.07
	48hrs, 6.5%	103.3 (17%)	silica	
1	1-2-0	101.6	orthosilicate	2.63
	2hrs, 6.5%			
Willemite		101.3	orthosilicate	2.0
Hemimorphite		101.8	disilicate	2.0

The Table shows the progression of formation on the zinc surface. Panel 1 shows the initial formation of a zinc orthosilicate species. As time progresses, the zinc disilicate became the predominate species on the surface as seen in panel 2. Also the presence of silica was seen in relatively low yields. As the reaction progresses, the relative amount of silica increased until it overshadows the whole spectra as seen in panel 4. The increasing amount of silica does not indicate a lower yield of zinc disilcate. The ESCA analysis in limited to the top 50 angstroms of a surface. The trend of the zinc to silicon ratio illustrated that there was an accumulation of silica as the ESCA did detect the zinc due to the increased levels of silica. Natural examples of orthosilicate and disilicate known as Willemite and Hemimorphite respectively, were tested for purposes of comparison. The binding energies show a 0.3 eV shift compared to the test panels. This was due to the presence of sodium ions which has been detected by ESCA. The presence of sodium ions decreased the covalency of the Si-O bond thus increasing the binding energy.

EXAMPLE 35

The purpose of this Example is to demonstrate using potentiodynamic (DC) polarization to measure corrosion resistance of a mineralized layer.

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5   The initial corrosion resistance on treated metal substrates (as described below in greater detail) were measured via the following electrochemical polarization method. The tests were performed utilizing a Solartron SI 1287 electrochemical interface connected to an electrochemical cell similar to that shown in ASTM-G5-87. The working electrode consisted of a 2 cm x 7.5 cm test panel held by a stainless steel alligator clip with copper wire attached to the

10   alligator clip. The assembly was maintained in a stationary position by holding the alligator clip tight against the end edge of a 13 mm inside diameter glass tube with the wire attachment running up the inside of the tube and the clamping lever arm extending outside of the tube. The tube was fitted to the glass flask by running it through a rubber stopper and the wire was held tight within the glass tube by running it through a rubber stopper at the top end of the glass tube.

15   The sample to be tested was positioned so that the alligator clip connection to the test panel does not contact the cell test solution. The counter electrode was a standard platinum electrode and the reference electrode was a standard saturated calomel electrode connected to the test cell via a salt bridge. Tests were performed at ambient lab conditions of 70 F.

The DC polarization tests were performed by adding 700 mL of 5.0 weight % sodium

20   chloride solution to the flask and aerating vigorously with compressed air for 30 seconds. The aeration rate was the reduced to bubbling at 60 mL per minute. The counter electrode, salt bridge, and reference electrode were then put in place. The sample substrate was prepared by applying a nonconductive, non-dissolving gel (Nyogel 759G, Nye Lubricants, Inc.) on the back, edges, and part of the front of the panel to leave a 2 cm x 2 cm test area uncoated for the polarization test.

25   Finally the test sample (working electrode) was placed in the cell and positioned approximately 2-3 mm from the tip of the salt bridge. The cell potential vs. Open circuit was monitored to determine when a steady value was reached (approximately 15-30 minutes) via monitoring by CorrWare for Windows, Version 1.4 software (Scribner Associates, Inc. Charlottesville, VA). After the steady state cell potential was achieved, a potentiodynamic polarization scan was

30   performed by scanning from -0.2 mV to +0.2 mV from the steady state cell potential(E_{corr}) vs. Open circuit potential. A scan rate of 10 mV/sec was utilized. The relatively fast scan rate was necessary to complete the anodic portion of the scan before enough zinc had dissolved from the surface to expose the underlying steel base material. The scanning software recorded one data point (current density in A/sq. cm) at each millivolt. Calculations were made utilizing CorrView

for Windows version 1.4 software (Scribner Associates, Inc. Charlottesville, VA) which both plotted the data (Potential in volts versus Log Current Density in A/sq. cm) , determined anodic (Ba) and cathodic (Bc) Tafel slope constants, and calculated the corrosion current (Icorr) density (intersection of the anodic and cathodic Tafel lines).

The following 4 samples were evaluated:

a). Panel #639 was an electrogalvanized steel panel (ACT E60 EZG 60G 2-side, clean, unpolished, 3"x6"x0.030") was rinsed with reagent alcohol and coated with a resin which consisted of:

80.5% by weight NeoRez R9637 (Zeneca Resins)

6.5 % by weight N grade sodium Silicate (PQ Corp.)

13.0% by weight water

The coating was applied with a standard #12 draw down rod followed by a 15 minute oven bake at 60 C. After allowing to cool for 10 minutes, the coating process was repeated to yield a dry film coating thickness of approximately 0.7 mils. After 570 days the panel was immersed in N-methyl-pyrollidone for 24 hours to dissolve coating. After light wiping , air drying, and reagent alcohol rinsing, a 2 cm x 7.5 cm section was cut off for potentiodynamic polarization testing.

b). Panel #4323 was an electrogalvanized steel panel (ACT E60 EZG 60G 2-side, clean, unpolished, 3"x6"x0.030") was rinsed with reagent alcohol and then with naphtha and coated with a gel of the following composition:

70.0 wt % Nyogel 759G (Nye Lubricants, Inc.)

10.0 wt % G Sodium Silicate (PQ Corp.)

10.0 wt.% Kasil ss-pwd Potassium Silicate (PQ Corp.)

10.0 wt.% Borogard ZB Zinc Borate (U.S. Borax)

The coating was applied with a gate type applicator to a thickness of 0.062 inches. After 107 days, the excess gel was carefully wiped off and the remaining thin film of gel was removed by spray-washing with naphtha with a solvent squirt bottle. The panel was allowed to air dry and then a 2 cm x 7.5 cm section was cut off for potentiodynamic polarization testing.

c.) Panel #4977 was an electrogalvanized steel panel (ACT E60 EZG 60G 2-side, clean, unpolished, 3"x6"x0.030") was rinsed with reagent alcohol and then wiped with a Kimwipe. A 3" x 4.5" area of the panel was then immersed in 800 mL of a solution of the following

5   composition:

10 wt. % N grade sodium silicate solution (PQ Corp.)

90 wt. % deionized water

The panel was connected as the cathode to a DC power supply (Leader model # 718-20D) and a potential of 6.0 volts was applied. The anode was a panel of the same type as the cathode with

10   the same area immersed in the solution (1:1 anode:cathode surface area), approximately 1.25 inches from the cathode. After 1 hour, the power supply was turned off and the panel was removed from solution. The panel was then air dried while hanging in a vertical position. After 24 days a 2 cm x 7.5 cm section was cut off for potentiodynamic polarization testing.

d.) An untreated an electrogalvanized steel panel (ACT E60 EZG 60G 2-side, clean,

15   unpolished, 3"x6"x0.030") was rinsed with reagent alcohol, wiped with a Kimwipe and then rinsed with naphtha and wiped with a Kimwipe and used as a control sample. A 2 cm x 7.5 cm section was cut off for potentiodynamic polarization testing.

The following results were obtained:

20

Sample #	Ecorr (Volts)	Icorr (A/sq. cm)	Bc	Ba
A	-1.0275	2.27876×10^{-6}	-0.142857	0.021357
B	-1.0491	8.15915×10^{-6}	-0.305985	0.027159
C	-1.0538	1.74087×10^{-7}	-0.058354	0.026380
Control	-1.0408	5.62732×10^{-5}	-0.809446	0.045221

The above results demonstrate that the aforementioned treatments produce a surface with a significantly lower corrosion_curent density (Icorr) value and thus are significantly more corrosion resistant.

25   EXAMPLE 36

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of galvanize metal

62

5   substrates. The interaction was detected by using ESCA analysis in accordance with

conventional methods.

Analytical conditions for ESCA:

10   Instrument   Physical Electronics Model 5701 LSci
           X-ray source   Monochromatic aluminum
           Source power   350 watts
           Analysis region   2 mm X 0.8 mm
           Exit angle*   50°
15   Electron acceptance angle   ±7°
           Charge neutralization   electron flood gun
           Charge correction   C-(C,H) in C 1s spectra at 284.6 eV

           * Exit angle is defined as the angle between the sample plane and the electron analyzer lens.
20

           Coatings were made up based on the ingredients and formulation methods shown in
Example 10. Different base oils and base oil combinations. alkali silicate types, silicate amounts,
and substrates were used to represent a cross section of possible ranges. The different base oils
comprised polyalphaolefin (polymerized 1-decene) and linseed oil. Two types of alkali silicates
25   were also used, sodium and calcium silicate. The concentration of the alkali silicate was also
varied from 1% to 50% wt to show the range of possible concentrations. Each set of coatings
were applied onto both cold rolled and galvanized steel panels.
           Each formulation was mixed together and applied onto the given substrate at a thickness
between 5 and 10 mils. The coatings were allowed to set for at least 24 hours and then removed
30   from the substrate. Removal was accomplished by first scraping off the excess coating. The
residual coating was washed with the base oil used in the formulation to absorb any of the silica
or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not
adequately removing the silica from the residual coating, will leave behind a precipitate in the
subsequent naphtha washing, making any surface analysis more difficult to impossible.
35

Formulations used for ESCA/XPS analysis

Sample #	1	2	3	4	5	6	7	8
Durasyn 174 wt.% (PAO)	49.3	44.3	49.3	44.3	87	79.2	70.4	44
Linseed Oil wt.%	49	44	49	44	0	0	0	0
Fumed Silica wt.%	0.7	0.7	0.7	0.7	12	10.8	9.6	6
Sodium silicate wt.%	1	10	0	0	0	0	20	50

Calcium silicate wt.%	0	0	1	10	1	10	0	0

ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. Higher binding energies (>103.8 eV) indicate precipitated silica due to the charging effect of the silica which has no chemical affinity to the surface. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

EXAMPLE 37

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of lead substrates. The interaction was detected by using ESCA analysis in accordance with conventional methods.

Coatings were made up based on the ingredients shown in table shown below. Different alkali silicate types and silicate amounts were used to represent a cross section of possible ranges. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 5% to 50% wt to show the range of possible concentrations. Each coatings was applied onto lead coupons. Prior to gel application, the lead coupons cut from lead sheets (McMasters-Carr) were cleaned of its oxide and other dirt by first rubbing with a steel wool pad. The residue was rinsed away with reagent alcohol and Kim wipes.

Each formulation was mixed together and applied onto a lead coupon at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.

Formulations used for ESCA/XPS analysis on lead panels

Sample #	1	2	3	4
Durasyn 174 wt.%	89	74	89	44
Fumed Silica	6	6	6	6

wt.%				
Sodium silicate wt.%	0	0	5	50
Calcium silicate wt.%	5	20	0	0

ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show some overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica. The primary binding energy for all of these samples were in the range of 102.1 to 102.3 eV.

EXAMPLE 38

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of GALFAN® substrates (a commercially available alloy comprising zinc and aluminum). The interaction was detected by using ESCA analysis in accordance with conventional methods.

Coatings were made up based on the ingredients shown in table shown below. Different alkali silicate types and silicate amounts were used to represent a cross section of possible ranges. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 5% to 50% wt to show the range of possible concentrations. Each coatings was applied onto galfan coated steel coupons. Prior to gel application, the galfan coupon, cut from galfan sheets (GF90, Weirton Steel), were rinsed with reagent alcohol.

Each formulation was mixed together and applied onto a lead coupon at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.

Formulations used for ESCA/XPS analysis on Galfan® panels

Sample #	1	2	3	4
Durasyn 174	89	74	89	44

65

wt.%				
Fumed Silica wt.%	6	6	6	6
Sodium silicate wt.%	0	0	5	50
Calcium silicate wt.%	5	20	0	0

5   ESCA was used to analyze the surface of each of the substrates. ESCA detection of the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The

10   metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show some overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

15   EXAMPLE 39

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of copper substrates. The interaction was detected by using ESCA analysis in accordance with conventional methods.

     Coatings were made up based on the ingredients shown in table shown below. Different

20   alkali silicate types and silicate amounts were used to represent a cross section of possible ranges. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 5% to 50% wt to show the range of possible concentrations. Each coatings was applied onto galfan coated steel coupons. Prior to gel application, the copper coupons cut from copper sheets (C110, Fullerton Metals) were rinsed

25   with reagent alcohol.

     Each formulation was mixed together and applied onto a lead coupon at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica

30   or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.

Formulations used for ESCA/XPS analysis on copper

35

Sample #	1	2	3	4
Durasyn 174	89	74	89	44

| wt.%				
Fumed Silica wt.%	6	6	6	6
Sodium silicate wt.%	0	0	5	50
Calcium silicate wt.%	5	20	0	0

ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show some overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

It is to be understood that the foregoing is illustrative only and that other means and techniques may be employed without departing from the spirit or scope of the invention as defined in the following claims.

THE FOLLOWING IS CLAIMED:

1. An amorphous mineralized surface comprising a cation and an inorganic oxide wherein the amount of oxygen is less than the stoicheometric.

2. A mineralized layer consisting essentially of the oxide network phase

$$A_x B_y O_z - nH_2O$$
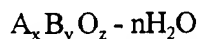
wherein A comprises a modifier cation comprising at least one member selected from the group of Group I, II and III metals, B comprises a network forming cation wherein the values of x, y and z are greater than 0. So long as the ratio of y:z is less than or equal to 4:1.

3. A transparent corrosion resistant mineralized layer comprising at least one phase obtained by contacting a silicate containing material with a metal surface at a pH ranging from about 9 to at least 11 wherein the amount of oxygen is less than stoichiometric.

4. The mineralized layer of Claim 3 wherein the metal surface comprises at least one member selected from the group consisting of iron, steel, zinc, magnesium, aluminum, vanadium, calcium, beryllium, manganese, cobalt, nickel, copper, brass, bronze, zirconium, thallium, chromium, and alloys thereof.

5. The mineralized surface of Claim 1 in which cations comprise one or more metals selected from the class consisting Group I, Group II, Group III, transition metals and rare earth metals of the Periodic Chart of the Elements.

6. The mineralized surface of Claim 5 in which the cations comprise an alkaline earth metal.

7. . The mineralized layer of Claim 2 in which anions comprise at least one member selected from the group consisting of selected from the group consisting of one or more of the anions selected from the group consisting of water soluble salts and/or oxides of tungsten, molybdenum, chromium, titanium, zircon, vanadium, phosphorus, aluminum, iron, boron, bismuth, gallium, tellurium, germanium, antimony, niobium (also known as columbium), magnesium and manganese, mixtures thereof, among others, and more especially, salts and oxides of silicon, aluminum and iron can be employed

8. The mineralized layer of Claim 4 wherein the metal surface comprises zinc and the silicate comprises sodium silicate.

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9. The mineralized layer of Claim 2 wherein the contacting comprises providing the silicate to the metal surface in the form of at least one member selected from the group consisting of a paint, coating or gel.

10. The mineralized surface of Claim 1 wherein the surface consist essentially of a complex oxide of the form:

$M_xN_yO_t$, wherein "M" represents one or more cationic elements having a covalency factor of less than about 0.5 that functions to balance the charge of the complex oxide, "N" represents one or more lattice forming elements having a covalency factor greater than about 0.15 that functions as the structural component of the complex oxide and optionally wherein the N_yO_t carries single or multiple crystal structures; and wherein x, y and t comprise any number the total of which balances the charge of the complex oxide.

11. The mineralized surface of Claim 10 wherein the covalency factor of M is less than about 0.33 and the covalency factor N is greater than about 0.33.

12. The mineralized surface of Claim 3 wherein the metal surface comprises zinc and the silicate comprises sodium silicate.

13. The mineralized surface of Claim 3 wherein the carrier comprises PAO or polyurethane and the silicate comprises about 1 to 30 wt.% of the carrier.

14. The mineralized surface of Claim 12 wherein the surface is heat treated at a temperature of about 125 to about 175 C.

15. The mineralized surface of Claim 1 wherein the Si(2p) photoelectron binding energy, measured by X-ray Photoelectron Spectroscopy, is higher than 102.1, but less than 103.3 eV, wherein the spectra identifies the mineralized species and wherein the binding energy is higher due to the accumulation of a silica oxide network.

INTERNATIONAL SEARCH REPORT

Intern nal application No.
PCT/US 98/01772

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09D 5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9612770 A1 (ELISHA TECHNOLOGIES CO.L.L.C.), 2 May 1996 (02.05.96), page 11, line 18 – page 12, line 2; page 20, line 1 – line 9, claims 1,9,16	1-15
X	US 5068134 A (JAMES A. COLE ET AL), 26 November 1991 (26.11.91), column 2, line 35 – line 50; column 3, line 59 – line 66, claim 1	1-15
X	US 4842645 A (SHIGEO MIYATA ET AL), 27 June 1989 (27.06.89), the claims	1-7,10-11

X	Further documents are listed in the continuation of Box C.	X	See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 May 1998	25. 06. 1998

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INTERNATIONAL SEARCH REPORT

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PCT/US 98/01772

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4645790 A (GARY T. FREY ET AL), 24 February 1987 (24.02.87), column 2, line 25 - line 34, claims 1-5	1-9
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X	DE 3618841 A1 (DAIMLER-BENZ AG), 31 March 1988 (31.03.88), column 1, line 37 - line 57, claims 1 and 5	1-13
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29/04/98

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